

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

Synthesis, crystal structure and catalytic activity of Guanidinium cation directed Nickel (II)-containing open Wells–Dawson 19-tungstodiarsonate (III) $[\{\text{Ni}(\text{H}_2\text{O})_4\}_2\{\text{Na}(\text{H}_2\text{O})\}\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{9-}$

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Mukesh Kumar Saini,^a Rakesh Gupta,^a Surendra Singh,^a and Firasat Hussain*^a

A new example of open Wells–Dawson type 19-tungstodiarsonate (III) $[\{\text{Ni}(\text{H}_2\text{O})_4\}_2\{\text{Na}(\text{H}_2\text{O})\}\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{9-}$ polyanion **1** has been synthesized in a single step reaction protocol, on interaction of nickel chloride with sodium salt of trilacunary $[\text{B}-\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ ligand in aqueous solution (pH ~5.8), in presence of pyridine-2,6-dicarboxylic acid. Guanidinium cation plays a structure-directing role to crystallize polyanion **1** as mixed salt of sodium and guanidinium salt in triclinic space group P-1. The solid state structure shows an open Wells–Dawson type $[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ anion containing two nickel atoms in octahedral geometry. Mixed sodium and guanidinium salt of polyanion **1** was further characterized by FT-IR, single crystal X-ray diffraction, thermogravimetric analysis, and vibrating sample magnetometry (VSM). Polyanion **1a** was screened as a catalyst for oxidation of styrene.

Introduction

Polyoxometalates (POMs) are molecular entities of early transition metal MO_6 ($\text{M} = \text{W}, \text{Mo}, \text{V}, \text{Ta}, \text{etc.}$) octahedra generally in their high oxidation states and main group XO_4 ($\text{X} = \text{P}, \text{Si}, \text{As}, \text{etc.}$) tetrahedra, forming a separate class of inorganic nanoclusters. POM compounds have some important properties like wide range of structural diversity (size and shape), flexibility, acidity, solubility, thermal stability, high charge density and redox stability, due to these intrinsic properties, POMs are thoroughly studied in the area of catalysis, medicine, molecular magnets, imaging techniques, biotechnology, and materials design.¹⁻¹⁰ Keggin and Wells–Dawson type POM nanoclusters are well known, but some other molecular entities like open Wells–Dawson, Anderson, and Preyssler type polyoxoanion are not much explored. The structural flexibility of POM compounds depends on size, shape and nature of the cation, number of vacant sites, and oxidation state of heteroatom (e.g. As^{III} vs As^{V}). As a result, synthesis of new POM complexes in open-air aqueous medium and the diversity in structural architecture with potential applications still remains an important research objective. Transition metal substituted POM compounds are important subclasses of metal oxide chemistry, among them lone pair containing As^{III} and Sb^{III} heteroatom containing sandwich type

complexes form a separate family for these subclass compounds. In this series, Robert et al. reported the copper containing $[\text{As}_2\text{W}_{18}\text{Cu}_3\text{O}_{66}(\text{H}_2\text{O})_2]^{12-}$ sandwich type polyanion, in which three Cu^{2+} ion are locked in the belt position and geometrically not in same environment.¹¹ Later, Kortz et al. reported a family of sandwich type complexes, as trisubstituted $[(\alpha\text{-XW}_9\text{O}_{33})_2\text{M}_3(\text{H}_2\text{O})_3]^{12-}$ ($\text{M} = \text{Cu}^{2+}, \text{Zn}^{2+}; \text{X} = \text{As}^{\text{III}}, \text{Sb}^{\text{III}}$) and disubstituted $[(\alpha\text{-AsW}_9\text{O}_{33})_2\text{WO}(\text{H}_2\text{O})\text{M}_2(\text{H}_2\text{O})_2]^{10-}$ ($\text{M} = \text{Co}^{2+}, \text{Mn}^{2+}$) polyanions.¹² Mean time Mialane et al. reported three sandwich type arsenato polytungstates $[\text{As}_2\text{W}_{18}\text{M}_3\text{O}_{66}]^{12-}$ ($\text{M} = \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}, \text{and } \text{V}^{\text{IV}}/\text{V}^{\text{V}}$), in addition they also reported two Ni(II) containing $\text{C}_8\text{K}_2[\text{Ni}(\text{H}_2\text{O})_6][\text{As}_2\text{W}_{19}(\text{H}_2\text{O})\{\text{Ni}(\text{H}_2\text{O})_4\}_2\text{O}_{67}]\cdot 17\text{H}_2\text{O}$ and $\text{K}_8[\text{Ni}(\text{H}_2\text{O})_6]_{1.5}[\text{As}_2\text{W}_{19}(\text{H}_2\text{O})\{\text{K}(\text{H}_2\text{O})\{\text{Ni}(\text{H}_2\text{O})_4\}\text{O}_{67}\}]\cdot 21\text{H}_2\text{O}$ POM compounds synthesized from dilacunary $\text{K}_{14}[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]$ precursor.^{13, 14} Drewes and coworkers, reported the structural characterization of Mn – containing sandwich-type $(\text{CH}_3)_4\text{N}[\text{Ni}(\text{H}_2\text{O})_6][\text{Mn}^{\text{III}}(\text{H}_2\text{O})_3(\text{SbW}_9\text{O}_{33})_2]\cdot 24\cdot 5\text{H}_2\text{O}$, $\text{Na}_{8.25}[(\text{Mn}^{\text{III}}(\text{H}_2\text{O})_2)_{2.25}(\text{WO}(\text{H}_2\text{O}))_{0.75}(\text{AsW}_9\text{O}_{33})_2]\cdot 28\text{H}_2\text{O}$, and $\text{Na}_3\text{K}_9[\text{Mn}^{\text{II}}(\text{H}_2\text{O})\text{Mn}_2(\text{AsW}_9\text{O}_{33})_2]\cdot 16\text{H}_2\text{O}$ complexes.¹⁵ Sandwich-type dititanium containing 19-tungstodiarsonate (III) $[\text{Ti}_2(\text{OH})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{8-}$ was also reported by one of us, and used as an oxidation catalyst.¹⁶

Hervé et al. discovered a new molecular entity $[\{K(H_2O)_3\}_2\{K(H_2O)_2\}(Si_2W_{18}O_{66})]^{13-}$, which was the first example of an open Wells–Dawson structure.¹⁷ This compound was used as a polydentate ligand and reacted with transition metals, which leads to the formation of new complexes with open Wells–Dawson structure, likewise $[\{Co(H_2O)\}\{Co(H_2O)_4\}\{K(H_2O)_2\}(Si_2W_{18}O_{66})]^{12-}$, $[\{M(H_2O)\}(\mu-H_2O)_2K(Si_2W_{18}O_{66})]^{13-}$ ($M = Co^{2+}, Ni^{2+}, Cu^{2+}$), $[\{M(H_2O)\}(\mu-H_2O)_2K\{M(H_2O)_4\}(Si_2W_{18}O_{66})]^{11-}$ ($M = Mn^{2+}, Co^{2+}, Ni^{2+}$), $[\{KV_2O_3(H_2O)_2\}(Si_2W_{18}O_{66})]^{11-}$ and $[\{Fe_4(OH)_6\}(Si_2W_{18}O_{66})]^{10-}$ polyanions.^{17–19} Later, Liu et al. reported the similar structural complexes with germanotungstates: $K_{13}[\{Co(H_2O)\}(\mu-H_2O)_2K(Ge_2W_{18}O_{66})\cdot 29H_2O]$ and $[\{M(H_2O)\}(\mu-H_2O)_2K\{M(H_2O)_4\}(Ge_2W_{18}O_{66})]^{11-}$ ($M = Co^{2+}, Ni^{2+}, Mn^{2+}$).^{20,21} To till date, no such open Wells–Dawson type structure are reported for lone pair containing heteroatoms. Herein, we report a new guanidinium cation directed nickel based open Wells–Dawson 19-tungstodiarisenate (III) $[\{Ni(H_2O)_4\}_2\{Na(H_2O)\}As_2W_{19}O_{67}(H_2O)]^{9-}$ (**1**) polyanion. The polyanion **1** has been synthesized by a single step reaction of nickel chloride with sodium salt of trilacunary $[B-\alpha-AsW_9O_{33}]^{9-}$ POM ligand in aqueous solution, in the presence of pyridine-2,6-dicarboxylic acid.

Experimental

Materials and methods

The trilacunary $Na_9[\alpha-AsW_9O_{33}]\cdot 27H_2O$ was prepared according to the published literature procedure and its purity was confirmed by FT-IR spectrum.²² All other chemicals were commercially purchased and were used without further purification. The Fourier transform (FT-IR) spectra were recorded with Perkin-Elmer BX spectrum on KBr pellets. The abbreviations used to define the peak intensities, s = strong, m = medium, w = weak, sh = shoulder. The UV/vis spectrum in solution was recorded by an Analytic Jena Specord 250 spectrometer. Thermogravimetric analysis (TGA) were performed using a TG/DTA instrument DTG-60 Shimadzu between temperature range of 25–700 °C in a nitrogen atmosphere with a heating rate of 5 °C/min. Elemental analysis data were collected from ICP-AES instrument, ARCOS from M/s Spectro Germany. Magnetic measurements were performed on a Micro sense ADE-EV9 magnetometer from -22 to 22 kOe applied magnetic field at room temperature.

$[C(NH_2)_3]_5Na_4[\{Ni(H_2O)_4\}_2\{Na(H_2O)\}As_2W_{19}O_{67}(H_2O)]\cdot 22H_2O$ (**1a**)

0.0713 g (0.3 mmol) of $NiCl_2\cdot 6H_2O$ was dissolved in 20 ml of H_2O with stirring. 0.0167 g (0.1 mmol) of pyridine-2,6-dicarboxylic acid was added in it, a light green solution was obtained. Solution was heated to 80 °C for 60 minutes and then 0.2464 g (0.1 mmol) of $Na_9[\alpha-AsW_9O_{33}]$ was added to the solution with continuous stirring. A clear green solution of pH 5.8 was obtained and cooled down to the room temperature, 1 ml of 0.5 M guanidinium chloride was added and the solution was left aside. After 2–3 weeks rod like green crystals were obtained, with a yield 0.1154 g, 46.3% (based on $Na_9[\alpha-AsW_9O_{33}]\cdot 27H_2O$). FT-IR: 1654(s), 946(m), 885(s), 792(sh), 746(s), 617(m), 501(m), 472(m), 441(w) (cm^{-1}). Elemental analysis (%); calcd (found): N 3.61 (3.52), Na 1.97 (1.86), As 2.57 (2.57), W 59.97 (59.87), Ni 2.02 (1.98).

Single crystal X-ray crystallography

A single crystal suitable for X-ray diffraction for compounds **1a** was mounted on a capillary tube for indexing and intensity data collection at 183(2) K on an Oxford Xcalibur Ruby CCD single-crystal diffractometer (MoK $_{\alpha}$ radiation, $\lambda = 0.71073$ Å).²³ Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the ABSCALE 3 program. Pre-experiment, data collection, data reduction and analytical absorption corrections²⁴ were performed with the Oxford program suite CrysAlisPro.²⁵ The crystal structures were solved with SHELXS-97 using direct methods.²⁶ The structure refinements were performed by full-matrix least-squares on F² with SHELXL-97.²⁶ All programs used during the crystal structure determination process are included in the WINGX software.²⁷ All heavy atoms (W, Ni, As) were refined anisotropically, The atoms (Na, O, C, N) are refined isotropically. The crystal data for the polyanion **1a** is summarized in **Table 1**.

A further detail on the crystal structure data may be obtained from CCDC 1033756 contains the supplementary crystallographic data for **1a**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk on quoting the depository number CCDC - 1033756.

Result and discussion

Synthesis and structure

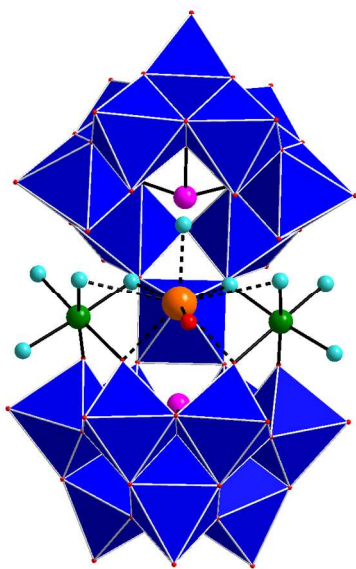
The title polyanion **1a** was isolated by the reaction of nickel chloride with trilacunary $Na_9[B-\alpha-AsW_9O_{33}]$ POM ligand in presence of pyridine-2,6-dicarboxylic acid in aqueous medium pH (~5.80). The starting materials were added in 3:1:1 molar ratio. Later, 1 ml of 0.5 M guanidinium chloride was added to the reaction mixture. Rod like green single crystalline material was collected after 2–3 weeks, and characterized as a mixed sodium – guanidinium salt of open Wells–Dawson type $[\{Ni(H_2O)_4\}_2\{Na(H_2O)\}As_2W_{19}O_{67}(H_2O)]^{9-}$ (**1**) molecular structure. Here the guanidinium cation plays an important role for the isolation of polyanion **1a**, whereas addition of caesium cation leads to the formation of $[\{Ni(H_2O)\}_2As_2W_{19}O_{67}(H_2O)]^{10-}$ polyanion, which was earlier reported by Mialane et al.¹⁴ Such observation was previously reported by Kortz et al.²⁸

The solid-state structure of the title polyanion **1a** reveals that the polyanion consists of two $[B-\alpha-AsW_9O_{33}]^{9-}$ Keggin units which connect to an extra $WO(H_2O)$ group, forming a dilacunary $[As_2W_{19}O_{67}(H_2O)]^{14-}$ anion type moiety.^{28, 29} In addition two nickel atoms and one sodium atom are coordinated to one of the $[B-\alpha-AsW_9O_{33}]^{9-}$ Keggin unit. Both the nickel atoms are coordinated to two different triads of $[B-\alpha-AsW_9O_{33}]^{9-}$ Keggin unit via μ_2 -oxo bridges (Ni–O–W), and also to sodium cation by μ_2 -dioxo bridges (Ni–O–Na), the presence of sodium cation in the centre of both the nickel atom bears two terminal aqua ligand, thus leading to a distorted octahedral geometry. The other $[B-\alpha-AsW_9O_{33}]^{9-}$ Keggin unit does not bond with nickel atoms but connect to nickel coordinated $[B-\alpha-AsW_9O_{33}]^{9-}$ Keggin unit via $WO(H_2O)$ group, where the tungsten octahedra act as an hinge, thus forming an open molecular structure having nominal C_{2v} symmetry. [see **Fig. 1**].

Table 1: Single crystal X-ray crystallographic data for compound **1a**

Empirical Formula	C ₅ As ₂ N ₁₅ Na ₂ Ni ₂ O ₉₁ W ₁₉
Formula weight	5532.59
Crystal system	Triclinic
Space group	P-1
<i>a</i> [Å]	13.1357(4)
<i>b</i> [Å]	16.6865(5)
<i>c</i> [Å]	26.3032(6)
α [°]	84.426(2)
β [°]	84.995(2)
γ [°]	66.972(3)
<i>V</i> [Å ³]	5273.2(3)
<i>Z</i>	2
ρ_{calcd} [g cm ⁻³]	3.484
μ [mm ⁻¹]	21.714
<i>F</i> ₀₀₀	4826
Reflections collected	211119
Unique (Rint)	20751
Observed [<i>I</i> > 2 σ (<i>I</i>)]	
Parameters	760
Gof	1.056
R [<i>I</i> > 2 σ (<i>I</i>)] ^[a]	0.0450
R _w (all data) ^[b]	0.1069

[a] $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$. [b] $R_w = \frac{[\sum w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^{1/2}}$

**Fig. 1** Ball and polyhedron representation of the polyanion $[\{\text{Ni}(\text{H}_2\text{O})_4\}_2\{\text{Na}(\text{H}_2\text{O})\}\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{9-}$. Color code: blue polyhedron: tungsten; green ball: nickel; pink ball: arsenic; orange ball: sodium; aqua ball: water molecule; red ball: oxygen.

The bond valence sum (BVS) calculations³⁰ show that both nickel atoms are present in +2 oxidation state and Ni(1)-O(68), Ni(1)-O(69), Ni(1)-O(70), Ni(1)-O(71) represents the four water molecules for Ni(1) atom, whereas Ni(2)-O(74), Ni(2)-O(75), Ni(2)-O(76), and Ni(2)-O(77) represents water molecules coordinated with Ni(2) atom. Two of the aqua ligand

coordinated to each nickel atom, are coordinated to sodium cation present at the centre.

Table 2: Selected bond distance (Å) for polyanion **1a**

C(1)—N(1)	1.38(3)	W(1)—O(6)	1.987(10)
C(2)—N(6)	1.33(2)	W(2)—O(9)	1.867(9)
C(3)—N(7)	1.31(2)	W(3)—O(25)	2.371(9)
C(4)—N(10)	1.29(2)	W(4)—O(25)	2.281(8)
C(5)—N(13)	1.36(2)	W(6)—O(17)	1.720(11)
O(1)—W(1)	1.710(12)	W(6)—O(18)	1.93(1)
O(4)—W(1)	1.975(10)	W(8)—O(21)	1.70(1)
O(7)—W(5)	2.079(10)	W(8)—O(27)	2.390(9)
O(8)—W(6)	2.108(10)	W(9)—O(25)	2.383(9)
Na(1)—O(39)	2.476(11)	W(10)—O(34)	1.72(1)
Na(1)—O(74)	2.497(11)	W(10)—O(35)	2.388(12)
As(1)—O(25)	1.789(9)	W(11)—O(42)	1.726(11)
As(2)—O(54)	1.800(9)	W(12)—O(45)	1.928(9)
Ni(1)—O(39)	2.062(9)	W(16)—O(72)	1.719(10)

The title polyanion **1a** closely resembles Mialane et al. reported cluster

$\text{K}_8[\text{Ni}(\text{H}_2\text{O})_6]_{1.5}[\text{As}_2\text{W}_{19}(\text{H}_2\text{O})\{\text{K}(\text{H}_2\text{O})\}\{\text{Ni}(\text{H}_2\text{O})_4\}\text{O}_{67}]\cdot 21\text{H}_2\text{O}^{14}$ but with structural differences. The title polyanion **1** is an open Wells–Dawson structure, while polyanion reported by Mialane et al. is a closed sandwich type complex. In polyanion **1** the two nickel atoms are coordinated to one of the $[\text{B}-\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ lacunary fragments with extra tungsten centre and a sodium cation, while one nickel atom with extra tungsten and a potassium cation is present in belt position of the polyanion reported by Mialane et al.

In the solid state structure of polyanion **1a**, the guanidinium cations present on the outer peripheral of the molecular cluster showing N-H...O_{POM} interactions of the guanidinium cation with terminal and bridging oxygen atoms of the polyanion [Fig. S1], and some interactions also with aqua ligands present in the crystal lattice. The H-bonding in between N3-H...O79(aqua), N5-H...O47(b), N6-H...O20(b), N7-H...O19(t), N11-H...O11(b), N15-H...O47(b) atoms, and the distances of these interactions are in the range of 2.777 – 3.057 Å [Fig. S2]. In the structure, N-H...O_{POM} interactions extended the POM unit in three-dimensional molecular structure [Fig. S1]. As a result, guanidinium cations are the essential requirement for the isolation of the polyanion **1a**, such structure directing influence of guanidinium cations was previously reported in literatures.^{31–35}

Infrared spectroscopy

The FT-IR spectrum of title compound **1a** [Fig. S3] shows four characteristic vibration bands centred at 946, 885, 792, and 746 cm⁻¹, which are assigned for $\nu_{\text{as}}(\text{W}-\text{O}_i)$, $\nu_{\text{as}}(\text{W}-\text{O}_b)$, $\nu_{\text{as}}(\text{As}-\text{O}_a)$, and $\nu_{\text{as}}(\text{W}-\text{O}_c)$ bonds, respectively.³³ The IR frequencies of title

compound are very similar to the $[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ anion on comparison, and these observations conclude that the trilacunary $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^9$ anion converts to the dilacunary $[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ anion during the course of reaction [Fig. S4]. The pH of the reaction mixture ~ 5.80 , is also evident for the transformation of POM ligand, reported in literature.³⁶ In addition three extra peaks are also observed due the presence of guanidinium cation. Two peaks centered at 3350 and 3173 cm^{-1} are assigned to NH_2 group, and a strong peak centered at 1654 cm^{-1} is attributed to C=N group, present in the guanidinium cation [Fig. S3].

UV-visible spectroscopy

The UV/vis spectrum [Fig. S5] for the polyanion **1a** was also recorded in aqueous solution and we observed two absorption bands in the spectrum, first stronger band at 191 nm is due $\pi\text{-}\pi^*$ charge transfer transitions of terminal oxygen atom (O_t) to d-orbitals of tungsten atoms, and a weak broad absorbance band around at 260 nm is due $\pi\text{-}\pi^*$ charge transfer transitions of $\text{O}_{(b,c)} \rightarrow \text{W}$ bonds present in the polyanion **1a**.

Thermogravimetric analysis

The thermogravimetric (TG) analysis of title compound **1a** was performed from room temperature to 700 °C under nitrogen flowing atmosphere with 5 °C/min heating rate [Fig. S6]. The compound shows four consecutive steps of weight loss due to crystal water molecules, guanidinium cation, and finally due to decomposition of the compound. The first weight loss step from room temperature to ~ 200 °C (9.73 %) corresponds to loss of 31 crystal water molecules. The second weight loss from 200 °C to 400 °C (6.3 %) corresponds to release of five guanidinium counter cations, later the compound starts decomposing from ~ 500 °C to 600 °C.

Vibrating sample magnetometry

Vibrating sample magnetometry (VSM) was performed for the title polyanion **1a** at room temperature, using Microsense ADE-EV9 vibrating sample magnetometer in the magnetic field from -22 to 22 kOe. A plot magnetization (M) versus applied magnetic field (H), which is named as M-H curve, is shown in Fig. 2. The compound shows paramagnetic behaviour and μ_{eff} value calculated from data was found to be 3.23 μ_{B} , which are in the range of observed μ_{eff} values for Ni^{2+} single ion. These suggest that no interaction phenomenon within the two nickel centre.

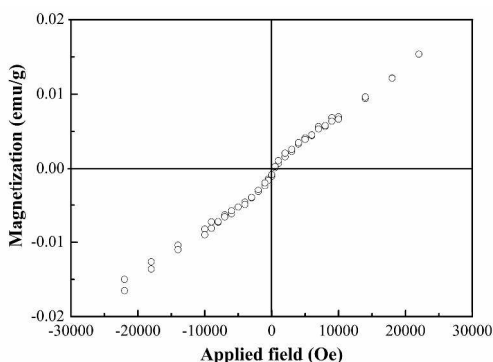
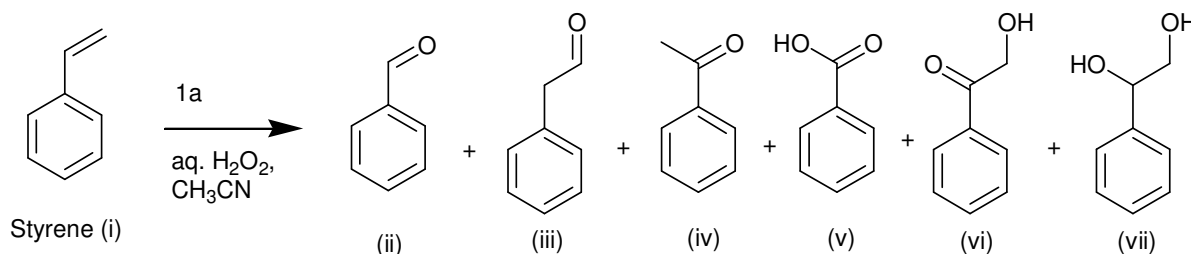


Fig. 2 Magnetization (M-H) curve of **1a** at room temperature.

Catalytic oxidation of styrene

The compound **1a** was tested as an oxidation catalyst for the oxidation of styrene in homogeneous medium. The catalytic reactions were performed by using styrene (2 mmol) as a substrate, catalyst **1a** (0.15 mol%), and aqueous H_2O_2 as an oxidant in acetonitrile solvent. The oxidation products of styrene were identified by comparing retention time on GC with their standard references and also confirmed by GC-MS. The results show (see Table 3) that at 60 °C temperature, H_2O_2 /substrate (4:1), 30% conversion of styrene was observed with 74% selectivity of benzaldehyde and remaining by-product's after 6h (Table 3, entry 1). When the temperature was increased to 70 °C for the same reaction conditions, conversion was improved to 50% and 72% selectivity of benzaldehyde was observed and further increase in temperature to 80 °C, conversion was increased to 82% and selectivity slightly reduced (Table 3, entry 3). The effect of oxidant (H_2O_2) was also investigated at 80 °C for the same reaction conditions, for H_2O_2 /substrate (3:1) that converted styrene to benzaldehyde in 83%, with 65% selectivity (Table 3, entry 3, 4 and 6). These results show that increase in H_2O_2 /substrate ratio from 2:1 to 3:1 conversion also increased but further increase in H_2O_2 /substrate ratio to 4:1, no change in conversion was observed. The conversion was also monitored at 3h and 9h for the reaction in which 3:1 (H_2O_2 /substrate) was used, to see the effect of time, we found that at 3h, 61% conversion was observed with 73% selectivity of benzaldehyde, and later at 9h, 94% conversion but with decrease in selectivity (59%) (Table 3, entry 5 and 7). The selectivity of benzaldehyde decreased with time due to aerial oxidation of benzaldehyde to benzoic acid. The reaction of styrene oxidation was also performed with POM $\text{Cs}_6\text{K}_2[\text{Ni}(\text{H}_2\text{O})_6][\text{As}_2\text{W}_{19}(\text{H}_2\text{O})\{\text{Ni}(\text{H}_2\text{O})\}_2\text{O}_{67}] \cdot 17\text{H}_2\text{O}$ reported by Mialane et al. and we found that 87% conversion was observed for oxidation of styrene, with 66% selectivity for benzaldehyde at 9h by using 3:1 (H_2O_2 /substrate) (Table 3, entry 8). Styrene oxidation was also carried out separately in presence of POM ligand $\text{K}_{14}[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]$ and also $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at 80 °C gives 34% and 11% conversions after 6h (Table 3, entry 9 and 10) respectively, these results are comparatively poor than the polyanion **1a**. In addition, the catalytic reaction was also performed in presence of both $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ salt and $\text{K}_{14}[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]$ POM ligand which gives slightly improved conversion (Table 3, entry 11), that suggests the molecular cluster polyanion **1a** shows better catalytic activity. Furthermore, the styrene oxidation was also performed using the reaction conditions mentioned in the very recently reported work³⁷ by Duarte et al. of known catalysts and we found 91% conversion was obtained in 6h and benzaldehyde was obtained as a major product with 60% selectivity (Table 3, entry 12), with other minor products. We have also studied the recyclability of the catalyst (see Table S1). The catalyst can be reused up to 2 cycles with gradual decrease in conversion of styrene.

ARTICLE

Table 3: Catalytic oxidation of styrene in presence of catalyst **1a** and aqueous H₂O₂.^a

Entry	H ₂ O ₂ /substrate	Temperature (°C)	Time (h)	Conversion (%) ^b	Selectivity for different products (%)					
					(ii)	(iii)	(iv)	(v)	(vi)	(vii)
1	4 : 1	60	6	30	74	3	12	-	11	-
2	4 : 1	70	6	50	72	2	11	4	11	-
3	4 : 1	80	6	82	68	2	10	6	14	-
4	2 : 1	80	6	52	71	2	7	5	15	-
5	3 : 1	80	3	61	73	2	12	3	10	-
6	3 : 1	80	6	83	65	2	12	8	13	-
7	3 : 1	80	9	94	59	2	8	13	18	-
8	3 : 1	80	9	87 ^c	66	2	8	10	11	3
9	3 : 1	80	6	34 ^d	76	5	10	-	9	-
10	3 : 1	80	6	11 ^e	94	-	6	-	-	-
11	3 : 1	80	6	36 ^f	72	6	10	6	6	-
12	4 : 1	80	6	91 ^g	60	3	11	12	14	-

^aReaction conditions: 2 mmol (styrene), 0.15 mol% **1a** catalyst, in 2 mL CH₃CN stirred for specified temperature and time. ^bConversion was determined by GC. ^cCs₈K₂[Ni(H₂O)₆][As₂W₁₉(H₂O){Ni(H₂O)₂O₆₇}]·17H₂O (0.15 mol%) was used as catalyst. ^dK₁₄[As₂W₁₉O₆₇(H₂O)] (0.15 mol%) was used as catalyst. ^eNiCl₂·6H₂O (5.0 mol%) was used as catalyst. ^fNiCl₂·6H₂O + K₁₄[As₂W₁₉O₆₇(H₂O)] (0.3 + 0.15) mol% used as catalyst. ^g1 mmol (styrene), 0.30 mol% catalyst **1a** in 3 mL CH₃CN.

Conclusions

In conclusion, we have isolated a new guanidinium cation directed nickel based open Wells–Dawson type polyanion with lone pair containing heteroatom $[\{\text{Ni}(\text{H}_2\text{O})_4\}_2\{\text{Na}(\text{H}_2\text{O})\}\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{9-}$ by a one pot reaction in aqueous solution pH 5.8. The title polyanion **1a** was structurally characterized by single crystal X-ray diffraction and other analytical techniques including FT-IR,

thermogravimetric analysis and VSM studies in solid state. Single crystal X-ray studies show that the title polyanion **1a** is an example of open Wells–Dawson anion, in addition the guanidinium counter cations act as a structure-directing agent. FT-IR spectroscopy shows the transformation of trilacunary $[\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ anion to dilacunary $[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ anion. VSM studies show the paramagnetic behaviour of title polyanion **1a** at room temperature in the presence of applied magnetic field. The polyanion **1a** was also screened as an oxidation catalyst for oxidation of styrene, and it shows good

catalytic conversion of styrene with prominent selectivity of benzaldehyde.

Acknowledgements

F. H. thanks University of Delhi, for R&D grant (ref: RC/2014/6820). We are grateful to Department of Chemistry, USIC, M.Tech NSNT, University of Delhi, for providing instrumentation facility and SAIF, IIT Bombay for ICP-AES.

Notes and references

^a Department of Chemistry, University of Delhi, North Campus, Delhi - 110007.

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

- M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, 1983.
- C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, 1995, **43**, 407.
- D. E. Katsoulis, *Chem. Soc. Rev.*, 1998, **98**, 359.
- B. Keita and L. Nadjo, *J. Mol. Catal. A: Chem.*, 2007, **262**, 190.
- Y. Zhou, R. L. Bao, B. Yue, M. Gu, S. P. Pei and H. Y. He, *J. Mol. Catal. A: Chem.*, 2007, **270**, 50.
- B. Hasenknopf, *Front. Biosci., Landmark Ed.*, 2005, **10**, 275.
- M. A. AlDamen, S. Cardona-Serra, J. M. Clemente-Juan, E. Coronado, A. Gaita-Ariño, C. Martí-Gastaldo and F. Luis, O. Montero, *Inorg. Chem.*, 2009, **48**, 3467.
- Z. F. Li, W. S. Li, X. J. Li, F. K. Pei, Y. X. Li and H. Lei, *Magn. Reson. Imaging*, 2007, **25**, 412.
- T. Yamase and M. T. Pope, *Polyoxometalate Chemistry for Nanocomposite Design*, Kluwer, Dordrecht, 2002.
- D. L. Long, E. Burkholder and L. Cronin, *Chem. Soc. Rev.*, 2007, **36**, 105.
- F. Robert, M. Leyrie and G. Hervé, *Acta. Crystallogr.*, 1982, **B38**, 358.
- U. Kortz, N. K. Al-Kassem, M. G. Savelieff, N. A. Al Kadi and M. Sadakane, *Inorg. Chem.*, 2001, **40**, 4742.
- P. Mialane, J. Marrot, E. Rivière, J. Nebout and G. Hervé, *Inorg. Chem.*, 2001, **40**, 44.
- P. Mialane, J. Marrot, A. Mallard and G. Hervé, *Inorg. Chim. Acta.*, 2002, **328**, 81.
- D. Drewes, M. Piepenbrink and B. Krebs, *J. Cluster Sci.*, 2006, **17**, 361.
- F. Hussain, B. S. Bassil, U. Kortz, O. A. Kholdeeva, M. N. Timofeeva, P. de Oliveira, B. Keita and L. Nadjo, *Chem. Eur. J.*, 2007, **13**, 4733.
- N. Laronze, J. Marrot and G. Hervé, *Chem. Commun.*, 2003, 2360.
- N. Leclerc-Laronze, J. Marrot and G. Hervé, *Inorg. Chem.*, 2005, **44**, 1275.
- N. Leclerc-Laronze, J. Marrot and G. Hervé, *C. R. Chimie.*, 2006, **9**, 1467.
- C. Y. Sun, S. X. Liu, C. L. Wang, L. H. Xie, C. D. Zhang, B. Gao, Z. M. Su and H. Q. Jia, *J. Mol. Struct.*, 2006, **785**, 170.
- C. L. Wang, S. X. Liu, C. Y. Sun, L. H. Xie, Y. H. Ren, D. D. Liang and H. Y. Cheng, *J. Mol. Struct.*, 2007, **841**, 88.
- M. Bösing, I. Loose, H. Pohlmann and B. Krebs, *Chem. Eur. J.*, 1997, **3**(8), 1232.
- Xcalibur CCD System, Oxford Diffraction Ltd, Abingdon Oxfordshire, England, 2007.
- R. C. Clark and J. S. Reid, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 1995, **51**, 887.
- CrysAlisPro* (versions 1.171.34.49), Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
- L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849.
- U. Kortz, M. G. Savelieff, B. S. Bassil and M. H. Dickman, *Angew. Chem. Int. Ed. Engl.*, 2001, **40**, 3384.
- C. Tourné and G. Tourné, *C. R. Acad. Sci. Paris Ser. C.*, 1975, **281**, 933.
- (a) I. D. Brown and D. Altermatt, *Acta Crystallogr.*, 1985, **B41**, 244; (b) N. E. Brese and M. O. Keefe, *Acta Crystallogr.*, 1991, **B47**, 192.
- S. Reinoso, M. H. Dickman and U. Kortz, *Eur. J. Inorg. Chem.*, 2009, 947.
- S. Reinoso, B. S. Bassil, M. Barsukova and U. Kortz, *Eur. J. Inorg. Chem.*, 2010, 2537.
- Q. Han, P. Ma, J. Zhao, J. Wang and J. Niu, *Inorg. Chem. Commun.*, 2011, **14**, 767.
- R. Al-Oweini, B. S. Bassil, T. Palden, B. Keita, Y. Lan, A. K. Powell and U. Kortz, *Polyhedron*, 2013, **52**, 461.
- F. M. Zonoz, I. M. Zonoz, A. Jamshidi and M. H. Alizadeh, *Solid State Sci.*, 2014, **32**, 13.
- L. G. Detusheva, L. I. Kuznetsova, L. S. Dovlitova and V. A. Likhobolov, *Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 370.
- T. A. G. Duarte, A. C. Estrada, M. M. Q. Simões, I. C. M. S. Santos, A. M. V. Cavaleiro, M. G. P. M. S. Neves and J. A. S. Cavaleira, *Catal. Sci. Technol.*, 2015, **5**, 351.